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PARAGENETIC ANALYSIS OF CARBONACEOUS ROCKS WITH SPURRITE-
MERWINITE FACIES

by V. V. Reverdatto

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An analysis is made of the paragenetic relationships of mineral carbonaceous rocks metamorphosed under high temperature and low pressure conditions in contacts of sub-igneous intrusions, chiefly of basic composition. The division of spurrite-merwinite sub-facies is based on two facies: the merwinite-calcareous, high temperature facies, and the monticellite-spurrite-tilleyite facies of relatively lower temperature.

Author

Marbles containing mineral phases not saturated with silica such as larnite, spurrite, randinite, merwinite, monticellite and others are metamorphic rocks which are formed under conditions of maximum temperatures and minimum pressures on the earth's surface. They are formed in exocontact aureoles of subvolcanic intrusions, chiefly of basic composition, and are rather rare mineral formations. In emphasizing the close spatial relationship of these products of metamorphism with volcanic rocks and their association with hornfels containing tridymite, mullite, sanidine, corundum, and others, P. Eskola referred to them as having sandinite facies [25, 26]; somewhat later, D. S. Korzhinskiy, using as a basis an analysis of natural parageneses and the law governing the relationship of the stability of calcium-magnesian mineral phases to the CO_2 pressure, proved the nature of the deposit by typomorphic minerals to be a larnite-merwinite facies of a depth characterized by low pressures and high temperatures [4]. U. Fife, F. Turner, and G. Ferhugen distinguish between two sub-facies within the sandinite facies of P. Eskola: 1) the larnite-merwinite-spurrite facies which corresponds to high temperatures and low pressures, and 2) the monticellite-melilite sub-facies corresponding to somewhat lower

temperatures and higher pressures [14, 16]. Recently, V. S. Sobolev refrained from using the phrase "sanidinite facies," quite correctly deeming it unfortunate;* and he proposed instead of distinguishing between the given spurrite-merwinite and monticellite-melilite facies, correspondingly the larnite-merwinite-spurrite and monticellite-melilite sub-facies of the sanidinite facies [13]. The division of the facies as proposed by Sobolev is adopted by the author of this article.

Doubts had often been expressed as to the possibility of achieving equilibrium in rocks of spurrite-merwinite facies [4, 14, 16]. Hence, the presence in them of unbalanced associations is sometimes regarded as a usual and quite normal phenomenon. However, this is apparently not so, although there are a number of reasons for the formation in the rocks of this facies of mineral associations which depart from equilibrium because the duration of metamorphism in the exocontact aureoles of subvolcanic intrusions was of considerably shorter than, for example, in regional processes of rock conversion in conditions of depth, the range of temperature variations being quite great. However, it should be mentioned that the time of maximum heating of the exocontact area in near-surface conditions, depending on the thickness of the magmatic body, its shape, and temperature and depth of occurrence is figured in years or tens of years (the body being of sufficient thickness) [3, 6, 32, 40], whereas the time necessary for the total realization of any reaction in the stability field of a terminal product in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$ system is not in excess of several hundred hours. But even this long reaction is characteristic only in the interaction of hard substances found in a thinly-dispersed and uniform mixture without the participation of CO_2 and H_2O .** The reactions with the

*The formation of sanidine in the hornfels of the facies in question points to the rapid cooling of rocks rather than to high temperatures, as a result of which feldspar preserves the disorder of the aluminosilicate framework.

**According to data provided by the author the reaction: 2-monticellite + spurrite-2merwinite + calcite (see below) is completed, practically speaking, in 400 to 500 hours at a temperature of 850 - 1000°C and one atmosphere of pressure. Apparently

participation of the latter progress considerably more rapidly [28, 50, 51], and the speeds of the reactions are greatly dependent on the pressure of the gas phase and temperature [2, 15, 16, 17]. Apparently in the case of a spurrite-merwinite facies the reactions with hard phases, with or without the presence of CO_2 , should be of rather great importance; the catalytic effect of H_2O is presumably excluded here [14]; in any case that is true at temperatures in excess of 1000°C . The speeds of diffusion which play a very important role in reactions with the participation of hard phases [2, 17], should not have an important effect on the speed of reaction of the substances involved and on the completeness of this reaction in the progressive metamorphism of a finely dispersed material of sedimentary rocks like siliceous limestone, dolomites and marl in which the reacting mineral phases are in very close contact along most of their surfaces and remind one in this regard of co-precipitated gels [16]. In the coarse grained initial material and in regressive changes in large crystal metamorphic rocks the substances react considerably slower [16], and the speed of the reaction and the reaction capacity of substances is markedly dependent on the degree of imperfection of the crystallic lattices of reacting

the mixture in which CaO is present in marked quantities reacts comparatively quickly. This fact was mentioned recently by A. Beretskiy [20]. However, even such reactions like, for example, the decomposition of diathene into mullite and quartz [16] and others are not so slow that the initial substances cannot pass over to a more stable condition in several years time under pressure and temperature conditions differing only slightly from the border of a phased equilibrium (with $T = 1090^\circ\text{C}$ and $P = 1 \text{ atm}$ —these conditions are apparently found in the vicinity of the border of phase equilibrium—the diathene changes completely into mullite and quartz in about three years [16]). Of course, we should take into account the fact that the reactions may be of a gradual nature, consisting of elementary, simultaneous or sequential reactions of intermediate products [15]; and with a slow rise in temperature the appearance of such intermediate phases (certain of them, possibly, are converted at the equilibrium phase limits of Bowen carbonate systems [21]) can actually affect the overall speed of reaction and retard the synthesis of the terminal product. However, as a rule, in contact metamorphism the temperatures rise very rapidly [3, 6] and all the intermediate phases appearing are of negligible dimensions; they are metastable in a progressive flow of the process and actually do not affect the overall speed and completeness of the reaction.

phases [15]. Nevertheless, there is no doubt that in the case of progressive metamorphism in a spurrite-merwinite facies the time factor cannot be an obstacle to achieving equilibrium in rocks (especially in the carbonates) that are subjected to high temperatures (up to 1000 - 1100°C) and pressures (up to 400 atmospheres).^{*} Very important also is the fact that natural mixtures are usually subjected to contact metamorphism; in the majority of cases they are relatively simple systems which are quite easily brought into a state of equilibrium [19]. Evidence in favor of the fact that equilibrium is attained in rocks with spurrite-merwinite facies is the continued observation of one and the same mineral parageneses (chiefly calcareous) in different exocontact zones, the comparatively rare occurrence in one sample of mutually excluding parageneses, etc. (see below).

At the present time there have been established in the world 20 manifestations of high temperature metamorphism of spurrite-merwinite facies^{**}. The rocks of this facies were first found by F. Wright in Velardina, Durango, Mexico, in 1908 [52]. During the past fifty years or so new discoveries of these rare and unique rocks were made in Crestmore, Riverside, California [22, 24, 33, 34]; on the Islands of Skye, Muck and Rhum and Cape Adnamurchan, Scotland [18, 30, 44, 46, 53]; in Scot Hill near Larna and Carlingford, Ireland [37-39, 43, 47, 48]; the Anakitsk Region on the Lower Tunguska River, USSR [9, 12]; in the Iron Mountains and the region of

^{*}This corresponds to depths of between 1500 and 1800 meters (if the pressure is governed entirely by the load of the overlying rocks).

^{**}We are not considering mineral parageneses occurring at high temperature metamorphism of non-carbone rocks (argillaceous shales and the like). Not too many of such rocks as the following have been found: hornfels of the Anakitskiy region [9], aluminiferous xenolites of hornfels from the tholeiites of the Island of Mall, sanidinites of Laakheraskoye Lake [14], and others. From the parageneses established in the hornfels the following are very characteristic: 1) anorthit-wollastonite-diopside-tridymite, 2) cordierite-anorthite-spinel, 3) anorthite-corund-spinel, 4) cordierite-spinel-mullite, 5) ferruginous wollastonite-hedenbergite [14] and others. The critical minerals in these associations which enable us definitely to class the rocks in which they are encountered as spurrite-merwinite facies are apparently only mullite and tridymite. The remaining minerals, as well as sanidinite, are stable within a broad band of temperatures. This does not permit us definitely to refer the sanidinites of Laakheraskoye Lake to the facies in which we are interested [14].

Tres Hermanas, New Mexico [27, 29]; Little Belt Mountains, Montana [41]; the Christmas Mountains, Texas [23]; Tocatoca, New Zealand [35]; Mallarajanahundi Nanjangud, Mysore, India [36]; Coahuila, Mexico [42]; Central Asia; the spurs of the Kuramin Range, USSR [1]; the Kochumdek River and the Kurymovka Delta of the Podkamennaya Tunguska River of the USSR [10]; and in the Yelkhovskiy Region of Bulgaria [31]. Unfortunately, most of the discoveries of spurrite-merwinite rock facies have not been thoroughly explored. In addition, many of them are characterized by a poor assembly of metamorphic minerals, and an extreme uniformity of mineral associations. Hence, in analyzing the paragenetic relationships between the minerals of this facies the author relied, primarily, on the factual materials from the well investigated contact zones of Scott Hill [43, 47, 48], Carlingford [37-39], Anakit [9, 12], the Island of Muck [44], and to a certain degree those of Crestmore [22, 24, 34].

The mineral parageneses appearing in the high temperature metamorphism of carbonate sedimentations have already been discussed in the work done by D. S. Korzhinskiy in 1937-1940 [4], N. L. Bowen [21], and S. E. Tilly [45]. D. S. Korzhinskiy made use of the data known at the time on the natural paragenesis and dry fusions of Rankin and Wright, and was the first to construct composite triangular diagrams of compositions—the paragenesis for spurrite-merwinite facies (larnite-merwinite abyssal facies). Utilizing these diagrams, he was able theoretically to predict the sequence of decomposition of calcium silicates with increased pressure of CO_2 ; in this manner, he noted certain laws in the change of mineral parageneses depending on the depth conditions [4]. Bowen somewhat later systematized the metamorphic reactions occurring in siliceous limestones and dolomites under conditions of increased temperature with constant pressure of CO_2 [21]. These reactions occur sequentially accompanied by progressive expulsion of CO_2 from the hard phases; as a result, there are formed the so-called "stages of metamorphism." "Each stage of

metamorphism is a successive stage of decarbonization" [21, page 235]. Bowen isolated a total of 13 such stages; three of the latter with which the sequential formation of spurrite, merwinite and larnite are related correspond to the spurrite-merwinite facies. On the basis of petrological consideration a number of composition diagrams were given for the stages of metamorphism—the paragenesis which included complicated accumulations of tri-mineral associations that follow one after the other progressively as the temperature increases. A well known supplement to the studies made by Bowen is the short contribution by S. E. Tilly dealing with the progressive metamorphism of carbonate rocks [45]. In it, certain parageneses of spurrite-merwinite facies are discussed, taking into account the later discovered minerals—tilleyite and rankinite. In recent years there has been an intensification in experimental studies dealing with the determination of the stability fields of various minerals formed at high temperatures and low pressures, and testing the aspects of "stages of decarbonization" by Bowen and others. Here, first of all, we should refer to the work of R. Harker, O. Tattle, L. Walter, I. A. Ostrovskiy, and others [8, 28, 49, 51].

In this article the analysis of paragenetic relationships in the spurrite-merwinite facies is made taking into account all the known mineral parageneses according to the method of D. S. Korzhinskiy [5], utilizing diagrams of chemical potentials of Al_2O_3 and CO_2 . In the diagrams, according to the rule of phases, there will correspond to the parageneses of five minerals non-variant points which are formed at the intersections of lines of univariant equilibrium which limit the stability field of tri-mineral paragenesis.

Contact-metamorphic marbles of spurrite-merwinite facies, as is well known, are characterized by associations which contain the following minerals: spurrite, merwinite, tilleyite, melilite, larnite, spinel, monticellite, rankinite, phlogopite,

periclase, forsterite, and wollastonite.* Rankinite and periclase are not considered in this article because the parageneses of the former have not yet been sufficiently studied,** and the parageneses with periclase are restricted to simple associations with calcite, spinel and forsterite [39] or with monticellite, spinel and calcite [44], and are of no particular interest. Forsterite likewise is not considered in associations of spurrite-merwinite facies because its parageneses are simple (usually they are encountered with periclase, monticellite, and spinel); they are observed rarely, and are most characteristic of monticellite-melilite rocks and hornfels facies of contact metamorphism.

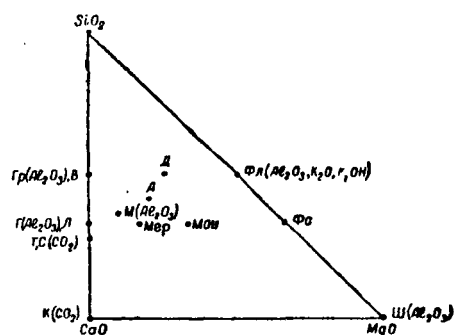


Fig. 1

Translator's note:

For key to Russian abbreviations on this and other Figures, see page 28.

Very characteristic of spurrite-merwinite facies are mineral parageneses of non-calcite contact-metamorphic rocks (it was established that larnite is unstable in associations with calcite [43] shown in Fig. 2. Serving as the original five-mineral parageneses in computing the corresponding clusters of lines of univariant

*The chemical formulas and symbols in diagrams for the minerals in the text and in the drawings are as follows: spurrite, $\text{Ca}_5\text{Si}_2\text{O}_{13}$ - C; tilleyite, $\text{Ca}_5\text{Si}_2\text{O}_{13}(\text{CO}_3)_2$ - T; helenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$ - Γ ; melilite, $1/2[\text{Ca}_2\text{Al}_2\text{SiO}_7] + 1/2[\text{Ca}_2\text{MgSi}_2\text{O}_7]$ - M; akermanite, $\text{Ca}_2\text{MgSi}_2\text{O}_7$ - A; larnite, Ca_2SiO_4 - Π ; spinel, MgAl_2O_4 - III ; calcite, CaCO_3 - K; merwinite, $\text{Ca}_3\text{MgSi}_2\text{O}_8$ - Mep; monticellite, CaMgSiO_4 - Mon; phlogopite, $\text{K}_2\text{Mg}_6\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH}, \text{F})_4$ - $\phi\pi$; diopside, $\text{CaMgSi}_2\text{O}_6$ - Π ; wollastonite, CaSiO_3 - B; forsterite, Mg_2SiO_4 - ϕ ; grossular, $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - Γp . The mutual disposition of phases in the concentration triangle $\text{CaO} - \text{MgO} - \text{SiO}_2$ is described in Fig. 1. Shown in parenthesis are the components which enter into the composition of the corresponding minerals in addition to the components at the vertices of the triangle.

**Typical of rankinite apparently is a paragenesis with larnite and other minerals in the absence of calcite [44, 45]. Associations of larnite-rankinite-spinel-helenite have been found on the Island of Muck [44].

equilibrium in this case were the stable natural associations of Scot Hill, Ireland, studied by S. E. Tilly: spurrite-helenite-merwinite-spinel-larnite [43] - [Mon] and helenite-spurrite-merwinite-spinel-monticellite [48] - [Л]. In analyzing this six-phase multisystem we first come to the conclusion that it is impossible for larnite to be formed in rocks containing a sufficient amount of alumina. Here, helenite becomes stable (at various μCO_2 for a given diagram [see Fig. 2]).

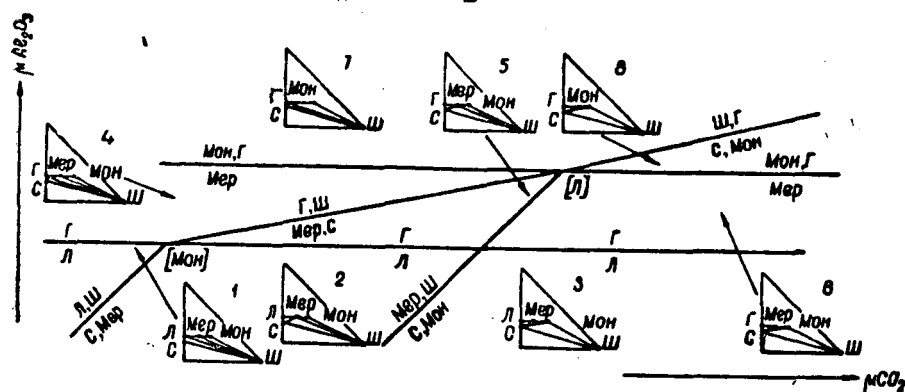


Fig. 2

Apparently this partially explains the rare occurrence of larnite in facies of spurrite-merwinite rocks (Scot Hill, the Island of Muck, Cape Ardnamerchan, Tokatoka) because the carbonate sediments subjected to metamorphism very often contain a certain amount of Al_2O_3 , i.e., in composition they approach marl or clay marl, whereas to form larnite relatively clear siliceous limestones are necessary. With small admixtures or shortages of alumina rocks may be formed which contain simultaneously larnite and helenite as, for example, on the Island of Muck, Scotland [44]. A similar picture is observed with respect to merwinite, which is also unstable in metamorphosing carbonate deposits enriched by a certain amount of Al_2O_3 , i.e., in rocks containing a relatively high $\mu\text{Al}_2\text{O}_3$ because the chemical potential of alumina in these conditions depends mainly on its concentration; in such rocks we find, simultaneously, monticellite and helenite (melilite) [44]. A characteristic peculiarity is noted in studying the parageneses with larnite as a function of the

magnitude of μ_{CO_2} : at low values of $\mu_{\text{CO}_2}^*$ it is possible to have three-phase paragenetic associations: larnite-spurrite-spinel and larnite-merwinite-spinel. At higher values of CO_2 the larnite is stable with merwinite and spurrite. An interesting relationship is noted also with respect to spurrite: at high values of CO_2 this mineral is stable with monticellite [1, 29], a fact that is not so at lower values of the chemical potential of CO_2 , i.e., at higher temperatures [9]. In the condition diagram (see Fig. 2) we also note the impossibility of paragenesis of larnite-monticellite; this is an important consequence of the stability of merwinite (without decomposition into Ca_2SiO_4 and CaMgSiO_4) right down to fusion temperatures [17].

Two diagrams Fig. 3 are devoted to the paragenesis chiefly of calcite containing metamorphic rocks of spurrite-merwinite facies, more carbonate than in the preceding case (of course, non-calcite paragenesis is possible here also). The original five mineral parageneses for the computation of two variants of multisystems of spurrite-spinel-calcite-merwinite-helenite-monticellite were associations taken from Scot Hill [47, 48], helenite, spurrite-spinel-merwinite. It is quite apparent that these associations are stable at different PT conditions, which is due to the reaction with the participation of four solid phases $\text{C} + 2 \text{Mon} = \text{K} + 2 \text{Mer}$. These four minerals cannot be present simultaneously in a divariant PT area. Hence, stable parageneses may appear with the participation of spurrite and monticellite at lower temperatures (Fig. 3a), or with the participation of merwinite and calcite at higher temperatures (Fig. 3b). Direct evidence of this is the example of a reactional replacement of the spurrite-monticellite aggregate with "subgraphical or vermicular" calcite-merwinite growths described by U. Burnham in a study devoted to the contact

*At high temperatures, if we have constant pressure and assume that it is determined mainly by PCO_2 and the partial pressure of water vapors does not play an essential role; the data used in the assumption are apparently quite real and fully acceptable in an analysis of high temperature metamorphism of carbonate rocks in a spurrite-merwinite facies [9, 16].

metamorphism of Crestmore [22, p. 906]. The main features which become apparent in an analysis of the condition diagram of a six-phase system (see Fig. 3) can be the following: instability of merwinite and spurrite at any values of a chemical potential of CO_2 in carbonate rocks rich in alumina (in which Al_2O_3 is relatively high); stability of parageneses of calcite-spurrite-spinel, spurrite-helenite-spinel, helenite-merwinite-spinel only at comparatively low values of μCO_2^* (an example of such parageneses are the associations of Scot Hill [43, 47] and the Island of Mack [44]); the overall increase in the number of possible three-mineral parageneses with calcite in the direction of an increased μCO_2 at all $\mu\text{Al}_2\text{O}_3$; the possibility of paragenetic associations of calcite-monticellite-spinel only at high values of μCO_2 . The last three-mineral association, as we can see, figures in both variants of the multi-system a and b Fig. 3 just like the typomorphic combinations of phases of devariant fields 1, 2, 8, and 9. However, as we have shown previously, the existence of two variations of a multi-system is due to the presence of mutually-excluding parageneses which are stable in various PT conditions. This leads to the conclusion that in the case at hand the above mentioned three-mineral parageneses are stable within a rather broad range of temperatures (and, apparently pressures), and the disappearance or appearance of either of these is determined mainly by the magnitude of μCO_2 and $\mu\text{Al}_2\text{O}_3$. It follows from this that a rough approximation of the existence of a functional relationship between the temperature and magnitude of μCO_2 at constant pressure is true only as a first approximation and should be used only in a preliminary evaluation of the physical conditions of metamorphism in the PT-region of spurrite-merwinite facies. This example demonstrates that in paragenetic conclusions we should take into account the relationship of μCO_2 not only to T or P but also to the concentration or activity of CO_2 and other components. The latter

*D. S. Korzhinskiy [4] pointed to the high temperature present in the paragenesis of spurrite with spinel compared with three mineral associations of calcite-merwinite-helenite. This conclusion finds support in the condition diagram 1b of the multi-system of Fig. 3.

is especially important in an analysis of the parageneses of rocks formed at similar or close temperatures and pressures. But in a rough evaluation of the conditions of metamorphism we can still utilize μCO_2 , as was previously done by D.S. Korzhinskiy [4], S. E. Tilley [45], and by the author [9], especially in delimiting the metamorphic facies by paragenetic associations, i.e., within comparatively broad variations in values of the chemical potential of CO_2 *

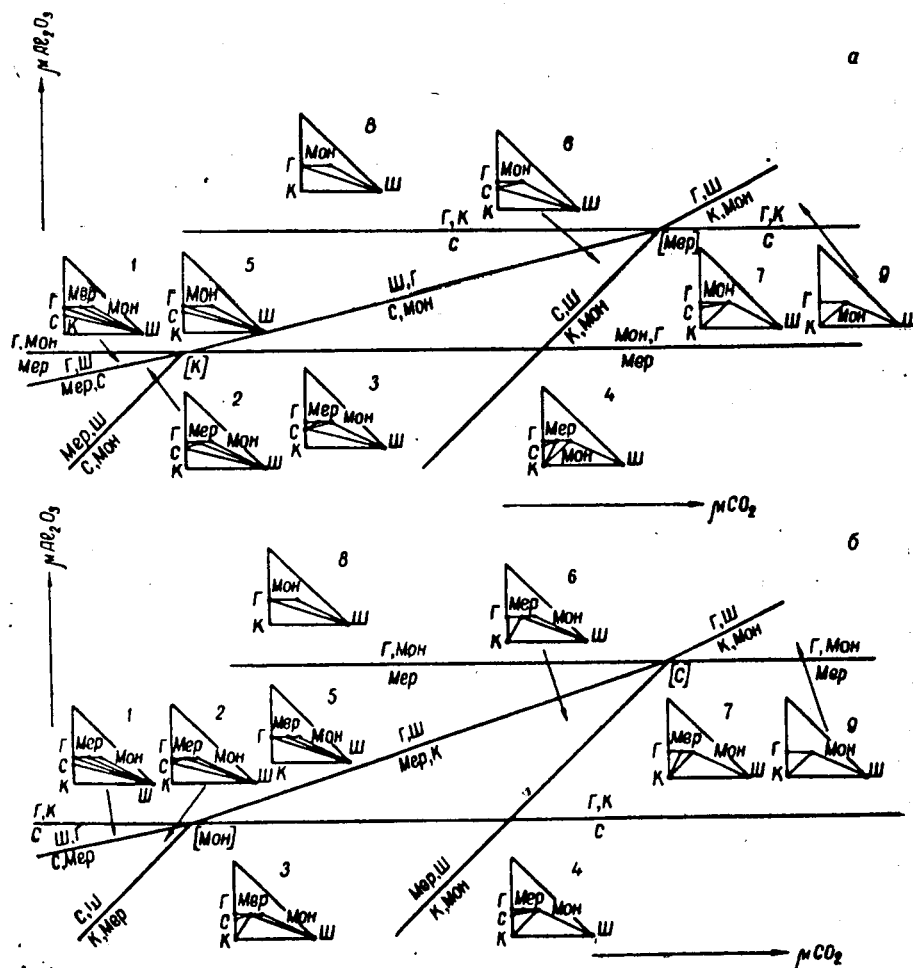


Fig. 3

Of great interest are the tilleyite-bearing marbles of spurrite-merwinite facies. Devoted to the analysis of the paragenetic associations of these rocks

*It is always important to take into account the assumption that in the case of metamorphism of carbonate rocks at shallow depths, the CO_2 pressure is constant [16, 21] and is determined, mainly, by the pressure of the load.

are three six-phased condition diagrams (Fig. 4). The first (I) and second (II) of them include parageneses with calcite, and the third (III) contains only non-calcite parageneses. The four-mineral paragenesis of calcite-spurrite-tilleyite-melilite (helenite) corresponding to the non-variation, non-spinel point of multi-systems I and II (Fig. 4) is encountered rather frequently in contact-metamorphosed limestones. It was established by S. Neckolds in the region of Carlingford [37], as well as by the author of this article in the region of the Kuzmovka Delta on the Podkamennaya Tunguska River [10] and on the Lower Tunguska River (Anakit). The non-tilleyite point of multi-systems III, as we have already indicated, corresponds to the stable five-mineral paragenetic association of Scot Hill [48]. In studying the data of the multi-system we note that in contrast to spurrite, which is unstable in carbonate rocks containing a sufficient amount of alumina, tilleyite at any μCO_2 is stable in metamorphosed deposits characterized simultaneously by high values of $\mu\text{Al}_2\text{O}_3$ and μCO_2 (i.e., at temperatures that are not excessive). Generally, the stability fields of spurrite and tilleyite are demarcated rather clearly (in the coordinates of $\mu\text{Al}_2\text{O}_3 - \mu\text{CO}_2$ and PT): spurrite is stable only at low μCO_2 while tilleyite is stable only at high μCO_2 (see below concerning lower temperatures). The reader's attention is also invited to the following peculiarity: tilleyite, like spurrite, apparently can be found in paragenesis with spinel (it is even possible to have a three-phase association of tilleyite-calcite-spinel); moreover, the most common association apparently, is a paragenesis of tilleyite (or spurrite) with monticellite and spinel; this is unstable, however, at very low μCO_2 or high $\mu\text{Al}_2\text{O}_3$ (at any μCO_2 for the diagram in question).

The six-mineral condition diagrams considered in the foregoing pertained, mainly, to parageneses formed at high temperature metamorphism essentially of limestone rocks containing an insignificant admixture of dolomite-marls, and siliceous, marlaceous, and dolomitic limestones. Several other associations appear in the

metamorphism of siliceous and marlaceous dolomites and dolomite marls. The rocks formed in this are characterized by the absence of spurrite, larnite, and tilleyite and by the extensive development of magnesian minerals of merwinite, spinel, monticellite, and melilite. In this case melilite has a rather definite composition: 40-50% of helenite component and 60-40% of akermanite component (sometimes, however, we have also observed very rich akermanite melilites in the Anakit Region [9], for example). In a paragenesis with spurrite, tilleyite and larnite, helenite usually does not contain over 10-20% of akermanite.

The six-phase multi-system of merwinite-monticellite-spinel-melilite-wollastonite-calcite in Fig. 5 is devoted to an analysis of the paragenetic association occurring in the metamorphism of essentially dolomitic deposits. The author does not know of any proved five-mineral paragenesis which could be used for constructing the system being analyzed. However, there is a rather large amount of factual material on four-phase natural associations which enables us with a high degree of probability to regard the conditions diagram shown in Fig. 5 as being stable. In particular, associations corresponding to the lines of uni-variant equilibrium which connect non-variant points [B], [L], and [Mer] are natural parageneses. There is no question about the stability of the associations: it is confirmed by the materials of the exocontact aureoles of Crestmore, Anakit and the Island of Muck [9, 22, 44]. D. S. Korzhinskiy has demonstrated the stability of the following four-mineral parageneses: calcite-melilite (helenite)-spinel-merwinite and calcite-monticellite-merwinite-spinel [4] on the basis of data provided by S. E. Tilley and certain theoretical considerations. Hence, it follows that at least two rays of a non-wollastonite node (of four whose stability has been proved) of the combination of phases under analysis should intersect at a point somewhere in the $\mu\text{CO}_2 - \mu\text{Al}_2\text{O}_3$ region. Consequently, a non-wollastonite node is stable because "all reactions which can occur between phases in a non-variant point can be determined by any two of them" [11, page 114]; the entire multi-system in Fig. 5 is also stable.

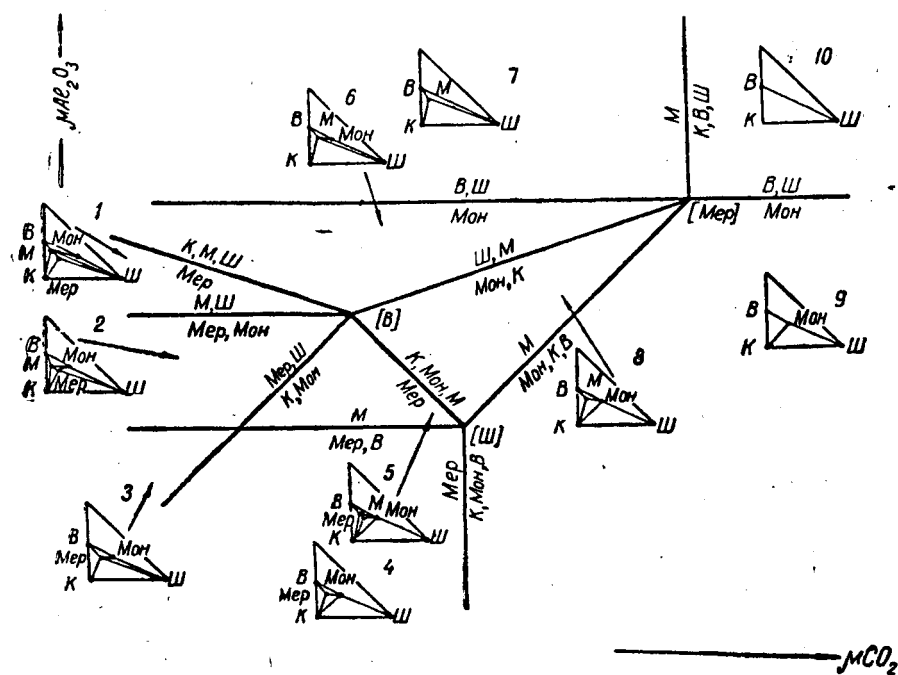


Fig. 5

Among the principal paragenetic conclusions resulting from an analysis of the diagrams in Fig. 5 one should note the fact that merwinite is stable only at low values of μCO_2 and $\mu\text{Al}_2\text{O}_3$, while monticellite is stable only in carbonate rocks that have a low alumina content at any μCO_2 (for the diagram in question). Melilite seems to be stable under conditions of high $\mu\text{Al}_2\text{O}_3$ and low μCO_2 . In rocks that are comparatively rich in alumina it is possible to have a paragenesis of melilite-spinel, as for example in the marbles of the Island of Muck [44]. Another peculiarity also is the impossibility of having a paragenesis of monticellite and calcite at low μCO_2 . Of particular interest is the question dealing with the stability of associations of monticellite and wollastonite. This paragenesis was doubted by N. Bowen in connection with the existence of associations of wollastonite-calcite-akermanite, akermanite-monticellite-calcite and the possibility of a reaction according to the system: $B + \text{Men} = A$ and $K + D = A + \text{CO}_2$ [21], as well as by Korzhinskiy on the strength of the possibility of such associations like wollastonite-merwinite-diopside, merwinite-diopside-monticellite, diopside-monticellite-spinel and diopside wollastonite-

helenite [4]. In other words, it appears that such a paragenesis is unrealistic in nature under any P and T conditions. However, the discovery by Tilley on the Island of Mull of rocks with a stable association of monticellite-wollastonite-melilite (melilite contains about 40% of akermanite component) and the direct detection of subgraphic aggregates of monticellite and wollastonite on the Island of Skye [46] and in the marbles of Crestmore where the minerals in question are encountered within the limits of the so-called "idocrase" zone in which merwinite is stable [22], prompts us to the conclusion as to the stability of the paragenesis in question under certain conditions. It is apparently possible at temperatures low for the spurrite-merwinite facies when a reaction $B + Men = A$ is still impossible. Generally, associations of monticellite-wollastonite are not characteristic of this facies (akermanite is stable here); it is more typical of lower temperature conditions. Still unclear is the question of the reality of the paragenesis of wollastonite-monticellite-merwinite at low values of μAl_2O_3 and μCO_2 . There is no doubt that at low values of the chemical potential of CO_2 , i.e., at high temperatures, merwinite is stable not with the above indicated minerals but with akermanite. In nature associations of merwinite with monticellite and wollastonite have not yet been determined, but it might be expected in the exocontacts of Crestmore. It is possible that this paragenesis is stable at very low CO_2 pressures and at temperatures which do not exceed the temperature of synthesis of akermanite in conformance with the reaction: $B + Men = A$. To determine this it is necessary to have additional field studies and experimental work to precisely define the field of stability of merwinite. Replacing parageneses containing merwinite and other minerals with parageneses containing monticellite, melilite and wollastonite is a transition from low pressures and high temperatures of spurrite-merwinite facies to somewhat lower temperatures and higher pressures of the monticellite-melilite facies (see Fig. 5). On further lowering the temperature (at constant pressure), monticellite and

melilite become unstable in conformance with the reactions of the seventh and eighth stages of Bowen: $D + Fo + 2K = 3 Mon + 2CO_2$ and $K + D = A + CO_2$ [21, page 250] or $3K + 3Sh + 3Er = 6 M + 3CO_2$, $K + 3B + Sh = 2M + CO_2$ and $K + B + Fo = 2 Mon + CO_2$ and so on. This means a transition to a hornfels facies of contact metamorphism.

A similar conclusion follows from the condition diagram [Fig. 6] which consists of seven-mineral multi-system (six phases of the previous multi-system and phlogopite). The initial five-mineral paragenesis observed under natural conditions for the diagram in question was the following association established by G. Osborne in Carlingford: monticellite-calcite-spinel-phlogopite-melilite [38, 39]. However, the stability of the node $[V, Mer]$ does not exclude the possible metastability of nodes $[V, III]$ and $[Mon, III]$ in the event of stability of the node $[Mer, III]$ (see Fig. 6), i.e., when the multi-system under consideration is reduced to a combination of six phases with the exclusion of merwinite. Hence, in order to avoid ambiguity in making and interpreting a condition diagram the author made use of information concerning the existence of stable three-phase parageneses: merwinite-melilite-phlogopite, in Little Belt Mountains [41]; monticellite-spinel-phlogopite in the northwestern Siberian platform [7]; and calcite-wollastonite-phlogopite in Crestmore and the Anakit [9, 22]. This diagram, just as in diagram 5, describes the mineral parageneses which appear in the metamorphism of essentially dolomitic deposits, but with small admixtures of potassium (and water). Paragenetic relationships reflected in Fig. 6 remind us in general about phenomena which have previously been set forth in an analysis of the multi-system in Fig. 5. The chief difference consists in the sharp reduction of the stability field of monticellite, which practically coincides here with the merwinite field, i.e., monticellite, like merwinite proves stable only at low values of μ_{CO_2} and $\mu_{Al_2O_3}$. The monovariant equilibrium line $Mon + Al_2O_3 = III$ and B on the diagram in question become metastable (shown by broken line). Our attention is directed to the very close relationship between spinel and phlogopite;

the paragenesis of spinel with melilite is possible only under conditions of high values of $\mu_{\text{Al}_2\text{O}_3}$ and comparatively low μ_{CO_2} .

In conclusion, we shall consider the relationship of mineral parageneses of spurrite-merwinite facies to temperature and pressure with an excess of CO_2 . For this purpose we shall construct a PT condition diagram with eight facies (a four component system: $\text{CaO-MgO-SiO}_2\text{-CO}_2$): spurrite, tilleyite, monticellite, akermanite, merwinite, wollastonite, calcite and CO_2 . The position of three lines of uni-variant equilibrium of the system in question: tilleyite = spurrite + CO_2 , 3 calcite + wollastonite = tilleyite + CO_2 and 2 merwinite + calcite = 2 monticellite + spurrite was rather precisely demonstrated through experimentation. The first two of them were studied by R. Harker [28] and the latter by L. Walter [49] and by the author of the present article. Because only hard phases take part in the equilibrium 2 merwinite + calcite = 2 monticellite + spurrite the uni-variant curve that corresponds to it should be very steep with respect to the temperature axis. This is actually the case. Walter found that the temperature of equilibrium is 820°C at atmospheric pressure and increases merely to 822°C at a pressure of 200 atmospheres. Similar data were obtained by the author in checking the experiment conducted by Walter. At $P = \text{atm}$ the temperature of equilibrium was equal to $825^\circ \pm 7^\circ$. All this enables us to regard the experimental material as reliable. The mutual disposition of the equilibrium curves is illustrated in the upper part of Fig. 7. It is apparent that the lines $2 \text{ mer} + \text{K} = 2 \text{ mon} + \text{C}$ and $\text{C} + \text{CO}_2 = \text{T}$ cannot but intersect at some non-variant point on the PT diagram. At the point which exists when $P = 80 \text{ atm}$ (pressure - CO_2) and $T = 825^\circ \pm 7^\circ$, 6 phases are simultaneously stable, and this means that the point is located at the intersection of six uni-variant equilibrium curves [11]. Two other six-nonvariant points are obtained when we have an intersection of the straight line corresponding to the equilibrium $\text{A} = \text{Mon} + \text{B}$ with uni-variant curves $\text{T} + \text{CO}_2 = 3\text{K} + 2\text{B}$ and $\text{C} + \text{CO}_2 = \text{T}$, the position of which in the PT region was

directed toward the region of high temperatures may possibly intersect with the curve: $2\text{Mer} + \text{K} + \text{CO}_2 = 2\text{Men} + \text{t}$, given a new six non-variant point, etc.* Univariant curves of R. Harker should in turn intersect somewhere at very low pressures and temperatures close to the limiting point for the spurrite-merwinite facies. Pointing to this conclusion is the repeatedly established paragenesis of wollastonite-spurrite-calcite. The association in question, corresponding to the equilibrium $3\text{K} + 2\text{B} = \text{C} + 2\text{CO}_2$ and established in Carlingford on the Island of Skye and in Coahuila, Mexico [37, 42, 53], are testimony to the thinning out of the tilleyite field in the area of low pressures. We can, of course, assume that the tilleyite field peters out at great pressures [4]. However, in that case the corresponding non-variant point would have to be placed in the region of pressures which, apparently, are not realistic for spurrite-merwinite facies (more than 500 atm). Guided by the foregoing considerations the author has constructed a diagram (Fig. 7). Not shown on it are certain univariant curves corresponding to the equilibria of hard phases (without CO_2): $3\text{Mer} + \text{T} + 2\text{B} = 2\text{C} + 3\text{A}$, $\text{Mer} + 2\text{K} + \text{A} = 2\text{Men} + \text{T}$ and others.** These equilibria, apparently, are not possible when there is an excess of CO_2 . In the equilibrium $\text{A} = \text{B} + \text{Men}$ it is essential to note the following. At high pressures of CO_2 akermanite breaks down not in conformance with the reaction in question but according to the system: $\text{A} + \text{CO}_2 = \text{D} + \text{K}$. But at such a low pressure of CO_2 akermanite has a common field of stability with calcite, and the paragenesis of akermanite (mellilite) with calcite is common in contact metamorphic marbles, especially under conditions of manticellite-melilite facies. Hence,

*There may be other variations in the construction of the diagram; for example, uni-variant lines corresponding to the equilibria $3\text{Mer} + 2\text{B} + 2\text{CO}_2 = 3\text{A} + \text{T}$ and $3\text{Mer} + 2\text{CO}_2 = \text{T} + \text{A} + 2\text{Men}$ can intersect with the equilibrium line for $\text{A} = \text{Men} + \text{B}$ and not with the $\text{C} + \text{CO}_2 = \text{T}$ line (shown by broken line in Fig. 7), but this does not cause any changes in the authors conclusions.

**Also not shown are the non-variant nodes without CO_2 .

continuation of a uni-variant line corresponding to the equilibrium $A = \text{Mon} + B$ into the region of relatively higher P_{CO_2} (up to a certain limit) appears logical.

The diagram (Fig. 7) appears very plausible and allows us to make certain paragenetic conclusions. First of all, it supports rather well the conclusion to the effect that it is admissible, with certain restrictions, to tie in the change in mineral parageneses observed in the rocks of ~~met~~excontact zones chiefly with changes in the temperature of metamorphism (with an excess of CO_2 and constant pressure). The natural parageneses are well laid down in an idealized system in Fig. 7 and we can consider it entirely realistic; it reflects the basic peculiarity of the metamorphism of carbonate deposits—the progressive decarbonation (sometimes regressive), usually at increased pressure (at constant temperature), or at a lowered temperature (at constant pressure). The diagram enables one to project the lower PT boundary separating spurrite-merwinite facies from the monticellite-melilite facies. Serving as this boundary, obviously, is the group of lines of uni-variant equilibrium: $3K + 2B = C + 2\text{CO}_2$, $3K + 2B = T + \text{CO}_2$ and $K + A = \text{Mer} + \text{CO}_2$. Below it, merwinite, spurrite, and tilleyite are unstable with an excess of CO_2 . At comparatively high pressures and temperatures the stability of merwinite goes beyond the limit of the stability fields of spurrite and tilleyite. Interesting to note is the division of the PT region of the spurrite-merwinite facies into two fields: the higher temperature field, where it is possible to have an association between merwinite and calcite in the presence of other minerals, and the lower temperature field in which is stable the paragenesis of monticellite-spurrite and (or) monticellite-tilleyite with merwinite (cf. Fig. 7). Serving as the boundaries between these fields are the lines of uni-variant equilibrium: $2 \text{Mer} + K = 2 \text{Mon} + C$, $2 \text{Mer} + K + \text{CO}_2 = 2 \text{Mon} + T$ and $\text{Mer} + \text{CO}_2 = K + A$. In the author's opinion along the boundary within the spurrite-merwinite facies we can distinguish two sub-facies with good basis for this: merwinite-calcite (high temperature) and the monticellite-spurrite-tilleyite

(relatively lower temperature) sub-facies. The overwhelming majority of manifestations of metamorphism of spurrite-merwinite facies known on the earth's surface pertains to the high temperature sub-facies. The low temperature sub-facies, which is characteristic mainly of the outer zones of exocontact aureoles, which are considerably rarer. In this sub-facies we can include the metamorphic rocks of Crestmore (outer, "monticellite" zone) [22], Gavasay, Central Asia, USSR [1], possibly Carlingford [37], and others. In this sub-facies the unbalanced associations should be more widely developed than in the higher temperature sub-facies.

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PARAGENETIC ANALYSIS OF CARBONACEOUS ROCKS OF SPURRITE-MERWINITE FACIES

Analysis of paragenetic relationship of carbonaceous rock minerals metamorphosed in conditions of high temperature and low pressure at the contacts of subvolcanic intrusions of dominantly basic composition is given in the paper. Some grounds are given for division of spurrite-merwinite facies into two subfacies: merwinite-calcitic, high-temperature one, and monticellite-spurrite-tilleyite, comparatively low-temperature one.

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Key to Russian abbreviations and symbols in figures.

<u>Cyrillic</u>	<u>Latin</u>	<u>Meaning</u>
В	V	wollastonite
Фo	Fo	forsterite
Л	L	larnite
Фл	Fl	phlogopite
Ш	Sh	spinel
Г	G	helenite
С	S	spurrite
Т	T	tilleyite
Гр	Gr	grossular
Мон	Mon	monticellite
Мер	Mer	merwinite
М	M	melilite
А	A	akermanite
Д	D	diopside